

A comparison of ethane, ethylene and CO₂ peel permeance for fruit with different coatings[☆]

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Abstract

Oranges, bell peppers and apples were treated with different coatings, and measurements were made of gas permeance through the peel. Shellac and wood resin coatings reduced ethane permeance of orange and apple peels by approximately 95% from the values for non-coated peel, and carnauba wax coatings gave about 85% reduction. The experimental procedure enabled us to make multiple measurements on the individual fruit CO₂ and ethylene production, internal gas concentrations and permeance. These measurements showed that some individual fruit were atypical in terms of CO₂ and ethylene production or permeance. Application of coatings resulted in some fruit having markedly high values of internal CO₂ and low O₂. High-barrier coatings not only caused large decreases in internal O₂ and increases in CO₂; but these also resulted in much larger variation in internal gas concentrations in different individual fruit with the same coating, much larger than the variation between different individual non-coated fruit. Because fruit quality is much dependent on internal gas concentrations, this means that high-barrier coatings result in fruit with higher variation in product quality.

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1. Introduction

The ease with which gases pass through the surfaces of fruits and vegetables is of considerable importance to preservation of quality. The O₂ required for normal

respiration must pass from the atmosphere through the peel in order to reach the inside of the fruit, and the CO₂ released by respiration must also pass through in order to escape the interior of the fruit. As is well-known, fruit and vegetables quickly become inedible and rotten when stored inside a barrier that blocks the supply of O₂ needed for respiration, and/or prevents the CO₂ produced by respiration from escaping. Such blockage lowers and raises the interior O₂ and CO₂ concentrations, respectively.

The quality of fruits and vegetables is affected in important ways by interior concentrations of gases. The control of quality changes by modified-atmosphere

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storage depends on regulation of environmental concentrations of O₂ and CO₂, which in turn affect their internal concentrations. Ripening and color of fruits is influenced by ethylene concentration. Flavor is dependent on the amount of volatile esters, alcohols, aldehydes and other compounds retained inside the fruit or vegetable. The efficacy of methyl bromide quarantine fumigation of the fruit interior depends on the amount of that gas that passes through the peel into the fruit interior.

It is well-known that barrier properties of peel are altered considerably by the washing and waxing that fresh fruits and vegetables undergo when prepared for marketing (Amarante and Banks, 2001; Hagenmaier and Baker, 1994). The natural waxes that serve as barriers to loss of water tend to be removed from the surface when the fruit is washed, resulting in more rapid dehydration. The coatings that are applied to apples and citrus fruit form barriers to the passage of O₂ and CO₂ through the fruit peel.

There are two ways to modify a peel to change its barrier properties, reflecting the two ways a gas can migrate through a barrier: (1) free diffusion through holes in the peel, such as lenticels, stomata, stem scars and injuries, and (2) *classical permeance*, which consists of a gas dissolving into a barrier on its high-concentration side, diffusing through the barrier, and coming out of solution on the low-concentration side.

The amount of gas passing through the peel by diffusion is proportional to the hole area, the coefficient of inter-diffusion of that gas into air, and the concentration gradient. The amount of gas passing through a barrier by *classical permeance* is proportional to the peel area, the gas solubility in the peel, the solid-state diffusion coefficient, and the concentration gradient. Cameron and Yang (1982) developed a procedure for using ethane to measure the barrier properties of tomato skin. This procedure consisted of holding the fruit in a container into which ethane is injected, then transferring the fruit to a second, ethane-free container and measuring the head space of that second container at different times. A newer method that involves measurement of internal gases was recently developed in our laboratory (Hagenmaier, 2004). For both permeance and diffusion the rate at which a gas passes through a barrier is proportional to the difference in concentration across the barrier. The rate of change of concentration

is proportional to concentration difference.

$$\frac{dC_{in}}{dt} = K (C_{out} - C_{in}) \quad (1)$$

where C_{out} is the gas concentration outside the fruit (but inside the container), C_{in} the internal gas concentration (the gas concentration inside the fruit) and t the exposure time (in min). The K value, which has units of t^{-1} , includes both diffusion and *classical permeance*, and is therefore dependent on peel area and hole area.

2. Materials and methods

2.1. Preparation of fruit

‘Valencia’ oranges were harvested in Polk county, Florida. Apples were from Washington, shipped courtesy of Publix Super Markets in refrigerated trucks to Winter Haven, Florida. The bell peppers were purchased from a grocer in Winter Haven. The coatings were obtained from manufacturers or made in our laboratory. The commercial coatings were two carnauba wax coatings (Brilliance from CH₂O Inc., Olmystia, WA and Natural Shine 9000 from Pace International, Seattle, WA), a shellac coating (APL-LUSTR 275 from Cerexagri, Monrovia, CA) and a resin coating (Sta-Fresh 590HS from FMC, Lakeland, FL). The coatings made in our laboratory consisted of a shellac coating (17.4% shellac, 2.6% morpholine, 0.9% food grade oleic acid [Emersol 6321 from Henkel Corp., Los Angeles, CA], 0.7% KOH, 0.5% propylene glycol, 0.5% polyethylene glycol 600, 0.007% polydimethylsiloxane antifoam, balance water), a carnauba wax coating (16.7% carnauba wax no. 3, 3.3% food grade oleic acid, 2.5% morpholine, balance water), and polyethylene (16.7% AC680 polyethylene [from Honeywell, Morristown, NJ], 3.3 % food grade oleic acid, 2.5% morpholine, balance water). A candelilla wax coating (18.6% candelilla wax, 2.3% food grade oleic acid, 1.1% myristic acid, 0.9% NH₃, balance water) that was made in the laboratory contained 22% total solids, and was used at that concentration or diluted with water as specified. The wax microemulsions made in our laboratory also contained about 0.002% polydimethylsiloxane antifoam [SE21 from Wacker Silicons Corp., Adrian, MI]. The fruit were coated by rubbing on the coating with gloved hands. Fruit were

weighed about 10 s before and again 10 s after application, to determine the wet weight of the coating applied. The mean amount of wet coating applied to oranges and apples was 0.32 g per fruit. For bell peppers the mean amount of liquid coating was 1.3 g for a candelilla coating with 22% total solids, and 0.6 g with other coatings. The coated fruit were stored at 20 °C, 60% relative humidity before measurement of internal gases and gas permeances at that same temperature. The duration of storage was 1 day, 1 week and 3 weeks for the bell peppers, apples and oranges, respectively.

2.2. Measurement of ethane gas permeance

The sample containers were cans of 4 L capacity, each connected to a diaphragm pump for recirculating the headspace gas at 2 L min⁻¹. Three to five fruit were put into a can, the pump started and sufficient hydrocarbon indicator gas (normally ethane, see Section 3) was injected into the can to bring the headspace concentration to about 300 µL L⁻¹ (0.03 kPa). Samples of the circulating gas were withdrawn at 5 min intervals for analysis. The can was opened, the exposure time recorded, and the fruit withdrawn immediately (within 5 s) to be submerged in water, and kept there for 1–4 min each until a sample of internal gas was withdrawn. For this method, C_{out} was virtually constant. Therefore, Eq. (1) integrates to

$$K = - \left[\ln \left(\frac{(C_{out} - C_{in})/C_{out}}{t} \right) \right] \quad (2)$$

The method involved direct measurement of C_{out} , C_{in} and t , and thus made for easy calculation of the K value. In order to calculate total quantity of gas passing through the peel, it is also necessary to know the internal gas volume of the fruit.

2.2.1. Internal gas volume

A partial vacuum was created inside the submerged fruit by removing about 1 ml of internal gas by syringe. A measured amount (100 µL) of a low-solubility marker gas (propane, butane or neon) was injected, the fruit kept submerged in water for 20 min, and an internal gas sample withdrawn to determine the internal concentration of the marker gas. For calibration, the same amount of marker gas was injected into 33.5 mL capacity glass vials. The gas volume of the fruit was

calculated as the amount withdrawn before injection plus

$$\text{Vol}_{\text{fruit}} = \frac{\text{Vol}_{\text{vial}} \times \text{Conc}_{\text{vial}}}{\text{Conc}_{\text{fruit}}} \quad (3)$$

Another method to determine internal gas volume was the removal of gas under vacuum. An individual fruit was placed in a beaker containing 2 L of recently He-purged water, positioned under an inverted 2 L plastic bottle with the bottom removed and closed at the neck with a rubber stopper fitted with a stopcock valve. After removal of gas from the inverted bottle the stopcock was closed and a vacuum applied (10 ± 0.3 kPa for 90 s). The gas captured under the bottle was removed within 2 min after release of the vacuum.

The production rates of ethylene and CO₂ were determined by placing fruit in closed containers for 2–4 h and monitoring increase in headspace concentration of these gases. The interior gas concentrations of ethylene and CO₂ were determined from measurement of interior gas concentrations. The permeance of CO₂ and ethylene through the peel were calculated by dividing the ethylene flux rates by the difference in concentrations of these gases inside and outside the fruit. The permeance of ethane was calculated as $K \times \text{Vol}_{\text{fruit}}$.

All permeance values were calculated per unit of surface area, to make for easy comparison, even though ‘hole’ area rather than surface area may be the determining value. Surface areas for oranges and ‘Fuji’ apples were calculated as $4\pi R_{\text{ave}}^2$ where R_{ave} was the mean radius of the fruit. Surface areas for bell peppers and ‘Red Delicious’ apples were determined by measuring the weight increase after covering the surface with tape of measured surface density.

2.3. Analysis of gases, statistics

The column used for analysis of O₂, CO₂, Ne and N₂ was the CTR I column (Alltech, Deerfield, IL), comprised of two concentric packed stainless-steel tubes, 1.8 m long, the outer tubing having 6 mm outside diameter and packed with an activated molecular sieve packing that irreversibly absorbs CO₂. The gas samples were injected using an 8-port dual external sample injector (Valco Instruments Co. Inc., Houston, TX). Loop capacity was 170 µL for internal gas samples. The detector and column temperatures were

120 and 70 °C, respectively, the column flow rate was 1.2 mL s⁻¹ (at 200 kPa). The gas chromatogram was a Model 5890 (Agilent Technologies, Wilmington, DE).

Samples of internal gas were taken from fruit held under water, using glass syringes with wetted barrels to hold the samples until injection into the gas chromatograph. In order to avoid contamination with atmospheric O₂, the syringe was previously flushed with N₂, and the tip fitted with a metal stopcock. Standard gases were injected before and after analysis of samples. Samples of room air were also analyzed regularly during the day.

The column used for analysis of ethane, ethylene, propane and butane was a Unibeads 2S 68/80, 1.8 m × 3 mm column operated at head pressure of 200 kPa and column flow of 1.0 mL s⁻¹. A gas chromatograph (Perkin-Elmer model Auto-System) was used with injection, oven and FID detector temperatures of 250, 115, 250 °C, respectively. Loop capacity was 50 µL for all measurements related to permeance constants, and 250 µL for measurement of ethylene production rates.

Data were analyzed with Statistics 7 (Analytical Software, Tallahassee, FL) using the Tukey test at $p < 0.05$ for comparison of means. In cases of multiple measurements on individual fruit, the first measurements were CO₂ and ethylene production, which do not involve puncturing the fruit. The fruit exposed to ethane and internal gases were measured for ethane uptake. Internal CO₂ and O₂ concentrations were also measured. Next, marker gases were injected and internal gases measured. Vacuum determination of internal gases followed. Finally, surface area was measured.

3. Results and discussion

3.1. Mean results for the treatments

The treatment means show that application of coatings drastically reduces the rate at which gases can pass through the coated peel of oranges and apples compared to uncoated, but not bell peppers (Tables 1–3). Compared to non-coated ‘Valencia’ oranges, those coated with a high-gloss, resin-based coating (HS 590) had ethane and CO₂ permeance reduced by 93 and 70%, respectively. The CO₂ permeance was less affected than the ethane permeance. Oranges coated with candelilla wax, carnauba wax or polyethylene wax had permeance values between those of non-coated fruit and fruit with the high-gloss coating. The values of internal O₂ and CO₂, were most different from environmental values (0.4% CO₂, 20.7% O₂) for the resin coating. The wax coatings reduced the mean internal O₂ by about 3–9 kPa and also reduced the CO₂ production rate to a value lower than that of non-coated control. The resin coating drastically lowered the internal O₂ to a mean value of only 0.2 kPa, which evidently was too low a concentration to support aerobic respiration, judging from the fact that this also increased the CO₂ production rate.

The results for apples followed the same trends, but with somewhat different results (Table 2). Compared to non-coated ‘Fuji’ apples, the application of shellac coatings reduced the values of ethane, ethylene and CO₂ permeance by about 95, 95 and 87%, respectively. The two carnauba wax coatings reduced these values somewhat less. For ‘Red Delicious’ apples the corresponding reductions were 84, 73 and 81%, respectively.

Table 1

Mean values of internal gases and barrier properties of the peel for ‘Valencia’ oranges stored at 20 °C with different coatings, $n = 15$

	Internal O ₂ (kPa)	Internal CO ₂ (kPa)	CO ₂ Prod (mmol kg ⁻¹ h ⁻¹)	Permeance (nmol m ⁻² s ⁻¹ Pa ⁻¹)		Permeance ratio (C ₂ H ₆ /CO ₂)
				C ₂ H ₆	CO ₂	
590 HS	0.2 a	22.0 a	0.70 a	0.02 a	0.11 a	0.16 a
Candelilla	6.1 bc	8.5 bc	0.31 b	0.05 ab	0.12 a	0.42 b
Brilliance	3.3 ab	14.0 b	0.39 b	0.05 ab	0.11 a	0.40 b
Polyethylene	9.0 c	6.6 c	0.40 b	0.11 b	0.24 b	0.44 b
No coat	13.5 d	5.3 c	0.53 ab	0.30 c	0.40 c	0.77 c

The application rate for all coatings was 3 g m⁻², dry weight basis. Mean values in the same column that are followed by different letters are significantly different ($p < 0.05$, Tukey).

Table 2

Mean values of internal gases and barrier properties of the peel for coated apples stored at 20 °C

Variety ^a	Coat ^b	Internal gas concentrations			Production rates		Permeance (nmol m ⁻² s ⁻¹ Pa ⁻¹)		
		CO ₂ (kPa)	O ₂ (kPa)	C ₂ H ₄ (Pa)	CO ₂ (mmol kg ⁻¹ h ⁻¹)	C ₂ H ₄ (μmol kg ⁻¹ h ⁻¹)	CO ₂	C ₂ H ₄	C ₂ H ₆
F	S	21.8 a	1.9 a	1.4 a	0.34 ab	0.3 a	0.07 a	0.02 a	0.01 a
F	AL	21.3 a	2.4 a	1.7 a	0.32 ab	0.5 a	0.07 a	0.02 a	0.01 a
F	C	9.5 b	5.5 b	2.6 a	0.26 a	1.5 a	0.10 a	0.05 a	0.03 a
F	B	8.8 b	2.9 ab	5.1 a	0.23 a	2.4 a	0.10 a	0.03 a	0.02 a
F	N	2.8 b	17.7 c	1.7 a	0.39 b	9.3 b	0.55 b	0.67 b	0.27 b
RD	AL	12.7 a	6.1 a	30.4 a	0.30 a	26 a	0.08 a	0.10 a	0.05 a
RD	C	8.2 b	10.6 b	31.4 a	0.41 ab	22 a	0.13 a	0.07 a	0.07 a
RD	N	2.6 c	17.5 c	9.2 b	0.45 b	24 a	0.49 b	0.06 b	0.22 b

Mean values for the same variety in the same column that are followed by different letters are significantly different ($p < 0.05$, Tukey).^a F: 'Fuji'; RD: 'Red Delicious'.^b S: shellac coating made in laboratory; AL: the shellac coating 'APL-LUSTR 275'; C: carnauba wax coating made in laboratory; B: the carnauba wax coating 'Brilliance'; N: no coating.

Table 3

Mean values of internal gases and barrier properties of the peel for bell peppers stored at 20 °C

	Internal CO ₂ (kPa)	CO ₂ production (mmol kg ⁻¹ h ⁻¹)	Permeance (nmol m ⁻² s ⁻¹ Pa ⁻¹)	
			C ₂ H ₆	CO ₂
22% Candelilla	2.1 a	0.77 a	0.43 a	0.79 a
16% Candelilla	1.6 a	0.70 a	0.40 a	0.93 a
10% Candelilla	1.9 a	0.77 a	0.41 a	0.88 a
10% Carnauba	2.0 a	0.68 a	0.27 a	0.65 a
No coat	1.6 a	0.69 a	0.42 a	0.95 a

Mean values in the same column that are followed by different letters are significantly different ($p < 0.05$, Tukey).

Table 4

Coating loads and weight loss at 60% RH, 20 °C

Fruit	Coating	Amount applied (dry basis) (g m ⁻²)	Weight loss	
			(% d ⁻¹)	As water vapor permeance (nmol m ⁻² s ⁻¹ Pa ⁻¹)
Fuji	Brilliance	3.9	0.11 c	11
	Carnauba	3.5	0.09 c	9
	Shellac	3.3	0.12 c	13
	APL LUSTR 275	3.8	0.15 b	15
	No coat	nil	0.18 a	18
Red Delicious	Carnauba	2.5	0.11 c	9
	APL LUSTR 275	2.6	0.16 b	11
	No coat	nil	0.20 a	13
	Natural shine 9000	3.4	1.0 b	42
Bell peppers	Candelilla (10%)	3.2	0.7 c	36
	Candelilla (16%)	4.9	1.0 c	53
	Candelilla (22%)	15	0.7 c	36
	No coat	nil	1.8 a	85

The values for the same variety in the same column that are followed by different letters are significantly different ($p < 0.05$, Tukey).

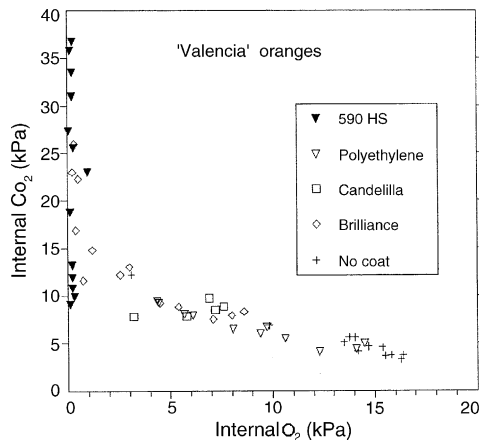


Fig. 1. Internal CO_2 and O_2 concentrations of individual 'Valencia' oranges with different coatings.

The mean internal O_2 values were not nearly so low as for the oranges.

For the bell peppers the only significant difference between coatings was weight loss, which was much reduced with candelilla wax coatings, even at fairly low concentration (Table 4).

3.2. Results from individual fruit

The internal CO_2 and O_2 values for individual oranges and apples showed a rather tight cluster of values for non-coated fruit, but a rather wide range for coated fruit (Figs. 1–3). A plot of internal O_2 versus internal ethylene for Red Delicious apples shows the

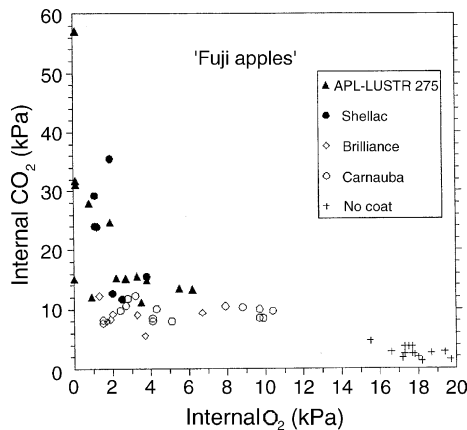


Fig. 2. Internal CO_2 and O_2 concentrations of 'Fuji' apples with different coatings.

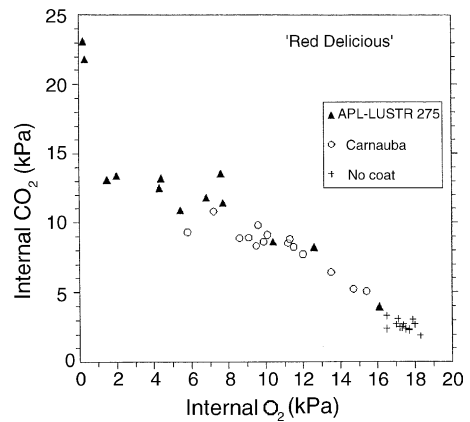


Fig. 3. Internal CO_2 and O_2 concentrations of 'Red Delicious' apples with different coatings.

same (Fig. 4). The internal gas values were particularly scattered for fruit with shellac and resin coatings, which caused the most reduction in peel permeance (Figs. 1–4). Compared to non-coated apples, lower internal O_2 and higher internal CO_2 internal gas concentrations for coated fruit are caused by the relatively lower permeance of the peel. The non-coated fruit had sufficiently high permeance that even individual fruit with unusually high values of CO_2 respiration or ethylene production showed relatively little change of internal gases.

Taking note of the fact that the difference between atmospheric and internal values of gas concentration is inversely proportional to the permeance constant,

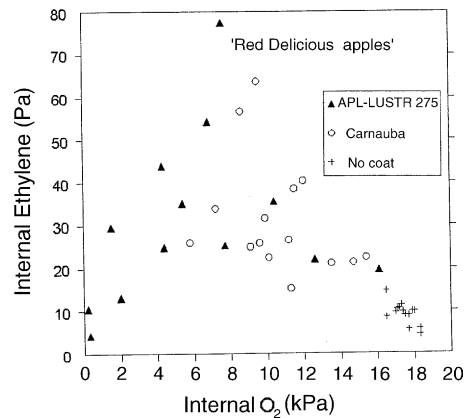


Fig. 4. Internal ethylene and O_2 of 'Red Delicious' apples with different coatings.

Table 5

Data for some individual 'Valencia' oranges, $n = 2$ for each measurement

Orange no.	Coating	CO ₂ production (mmol kg ⁻¹ h ⁻¹)	Internal gas concentration (kPa)		Permeance (nmol m ⁻² s ⁻¹ Pa ⁻¹)	
			CO ₂	O ₂	CO ₂	C ₂ H ₆
1	590 HS	0.31	11.9	0.2	0.10	0.01
2	590 HS	0.47	18.8	0.1	0.11	0.01
3	590 HS	1.23	36.7	0.2	0.13	0.02
4	Brilliance	0.34	7.5	7.1	0.16	0.06
5	Brilliance	0.33	13.0	3.0	0.09	0.06
6	None	0.45	3.3	16.3	0.51	0.29
7	None	0.75	12.2	3.1	0.22	0.11

it follows that a 95% decrease in permeance causes a 20-fold increase in internal gas (CO₂). This underscores the importance of gas permeance of the peel, since it is well-known that the quality of fresh citrus fruit, like that of many other fruits and vegetables postharvest, is much affected by the internal concentrations of CO₂ and O₂ (Ahmad and Khan, 1987; Ke and Kader, 1990; Hagenmaier, 2002). The effect of coatings on fruit is sometimes difficult to understand from mean values of internal gases and permeance, or from plots like Figs. 1–4 that only show two measurements on each fruit (two fruit with 2 measurements/fruit). Consider now a few individual fruit in more detail (Tables 5 and 6). The reason resin coated oranges #1, 2 and 3 had considerably different internal CO₂ concentrations (12, 19 and 37%, respectively) can be explained by their different CO₂ respiration values (0.31, 0.47 and 1.23 mmol kg⁻¹ h⁻¹, respectively, Table 5). In contrast, the reason oranges #2 and 6 had different internal CO₂ values (19 and 3%, respectively) seems to be the large difference in CO₂ permeance (0.11 and 0.51, respectively). Oranges #1 and 7, which had quite dif-

ferent respiration rates (0.21 and 0.75 mmol kg⁻¹ h⁻¹, respectively) had almost the same internal CO₂ (11.9 and 12.2 kPa, respectively) because the peel of orange #7 was more permeable, thus permitting the CO₂ easier escape. In contrast, oranges #4 and 5 had almost the same respiration rates but quite different internal CO₂ concentrations (7.5 and 13.0 kPa, respectively) because of differences in permeance.

Consider also some data for individual apples (Table 6). Apple #2 had about eight times the ethylene production of apple #1. The internal ethylene concentration was also about eight-fold different because the fruit had similar permeance values. By contrast, apples #1 and 4 had about the same internal ethylene, despite the much higher ethylene production of #4, because the much higher permeance of #4 allowed ethylene to escape more easily. Likewise, the higher peel permeance of #6 explains why it had about the same internal CO₂ and C₂H₄ concentrations of #5, despite its much higher CO₂ and C₂H₄ production rates. The reason for large fruit-to-fruit differences in permeance are most likely caused by variability in breaks in the peel. How

Table 6

Data for some individual apples stored at 20 °C

Apple no.	Type ^a	Coat ^b	Internal CO ₂ (kPa)	Internal C ₂ H ₄ (Pa)	Production rates		Permeance (nmol m ⁻² s ⁻¹ Pa ⁻¹)			
					CO ₂ (mmol kg ⁻¹ h ⁻¹)	C ₂ H ₄ (μmol kg ⁻¹ h ⁻¹)	CO ₂	C ₂ H ₄	C ₂ H ₆	H ₂ O
1	F	AL	15.6	1.1	0.35	0.26	0.08	0.04	0.02	15.5
2	F	AL	11.2	9.7	0.24	2.01	0.08	0.03	0.02	14.7
3	F	AL	24.7	1.3	0.39	0.12	0.06	0.01	0.01	13.2
4	F	N	2.6	1.1	0.38	8.2	0.55	1.13	0.34	17.9
5	RD	C	8.3	63.7	0.11	12.9	0.03	0.02	0.03	6.5
6	RD	C	8.9	56.7	0.38	36.7	0.11	0.07	0.05	7.4

^a F: 'Fuji'; RD: 'Red Delicious'.^b AL: APL-LUSTR 275, C: carnauba wax coating, N: no coating.

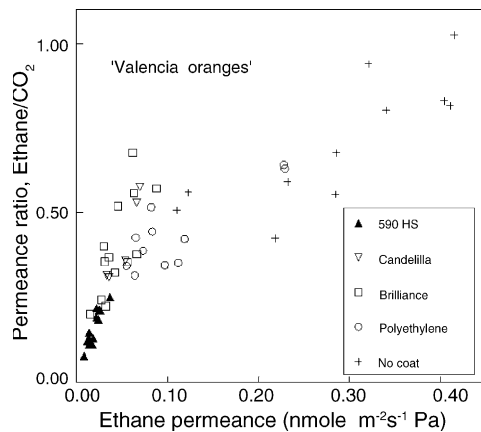


Fig. 5. Ratio of permeance (ethane/CO₂) to ethane permeance for 'Valencia' oranges.

the production rates and internal gas concentrations of these samples relate to one another can only be understood by using measurements on the same fruit. Had the internal gases been measured on one fruit and the production rate on another, the differences would have looked like experimental error.

The ethane and CO₂ permeance for oranges and apples seem to be related (Figs. 5–7). The high-barrier coatings (shellac and resin-based) tend to have lower ratios of ethane to CO₂ permeance than non-coated fruit, suggesting that there may be a different mechanism of permeance for coated fruit. The logic is as follows. When diffusion is the primary mechanism, little difference is expected for different gases, the gaseous diffusion constant being rather similar (Table 7). However, the rates of *classical permeance* of gases through the same membrane are normally quite different. For example, for 21 plastic films, the mean *classical permeance* of CO₂ was 4.3 times the O₂ permeance with a range of 2.7–6.6 times (Stannett, 1985). A ratio of about 4:1 also applies to many other films (Anonymous,

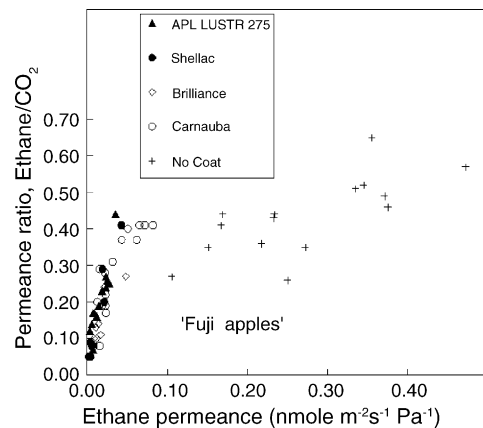


Fig. 6. Ratio of permeance (ethane/CO₂) to ethane permeance for 'Fuji' apples.

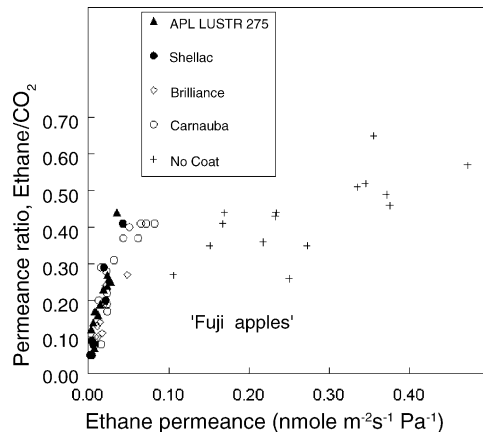


Fig. 7. Ratio of permeance (ethane/CO₂) to ethane permeance for 'Red Delicious' apples.

1995). This suggests the possibility that some coatings block enough pores, that *classical permeance* becomes the dominant mechanism for passage of gases through the peel.

Table 7

Calculated intermolecular diffusion constants for diffusion into nitrogen at 20 °C

	CO ₂	O ₂	C ₂ H ₆	C ₂ H ₄
Literature value of van der Waals constant b (mL) ^a	42.7	31.8	63.8	57.1
The atomic diameter calculated from b (Angstroms) ^b	3.24	2.94	3.70	3.57
Intermolecular diffusivity with N ₂ calculated from the diameter (cm ² /s) ^c	0.208	0.234	0.188	0.199

^a Values from Weast, 1976. The van der Waals b value is equal to four times the molecular volume (Glasstone, 1946).

^b Calculated assuming that Avogadro's number of spherical molecules has a volume of 1/4 of the van der Waals constant.

^c Calculated from equation no. 5–64 (Hecht, 1990).

The data show other evidence that the rates at which different gases permeate or diffuse through the peel are not easily related to one another. The mean ratio of ethylene permeance to ethane permeance for all individual apples was about the same for all coatings; the mean value was 2.2 ± 0.5 . The expected ratio for diffusion through holes would be about 1.06, calculated as $0.199/0.188$, the ratio of their intermolecular diffusivities in air (Table 7).

The effect of coatings on water loss is a well-known example of how coatings differently affect barrier properties of peel. Weight loss data converted to the same units as those used for peel permeance to CO_2 , C_2H_4 and C_2H_6 , showing that water vapor permeance of the peel is much larger and differently affected by coatings than is permeance to other gases. For example, water vapor permeance was decreased from 0.85 to $0.36 \text{ nmol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ by application of 22% candelilla wax coatings to bell peppers (Table 4), while at the same time the ethane permeance was unchanged (Table 3). Application of shellac to Fuji apples only decreased the water vapor permeance of Fuji apples by about 30%, but it decreased the values for C_2H_4 and CO_2 permeances by 97 and 87%, respectively (Table 2).

It would be interesting to know how coatings decrease peel permeance for methyl bromide and to evaluate how rapidly its internal gas concentration rises during fumigation of fresh fruit. This, however, would be difficult to measure because of the relatively larger solubility of methyl bromide in water compared to ethane, which means little methyl bromide remains in the gas phase after its passage through the peel into the wet interior of the fruit.

3.3. Fruit internal gases

In the course of measuring ethane resistance, measurements were also made of fruit weight and interior

gas volumes. The individual volume: weight ratios were used in the calculations. The mean values may be of interest for other purposes (Table 8).

4. Conclusion

Application of shellac or resin coatings resulted in large decreases in gas permeance and/or diffusion of fruit peel, possibly because of blockage of holes. These same coatings resulted in large decreases in internal O_2 and increases in CO_2 , and also much variation in internal gas concentrations in different individual fruit with the same coating, much larger than the differences between different individual non-coated fruit. Because fruit quality is dependent on internal gas concentrations, this means that low-permeance coatings result in fruit with higher variation in product quality.

References

- Ahmad, M., Khan, I., 1987. Effect of waxing and cellophane lining on chemical quality indices of citrus fruit. *Plant Food Human Nutr.* 37, 47–57.
- Amarante, C., Banks, N.H., 2001. Postharvest physiology and quality of coated fruits and vegetables. *Hort. Rev.* 26, 161–238.
- Anonymous, 1995. Permeability and Other Film Properties of Plastics and Elastomers. *Plastics Design Library*, Norwich, NY, pp. 509, 522, 525 and 575.
- Cameron, A.C., Yang, S.F., 1982. A simple method for the determination of resistance to gas diffusion in plant organs. *Plant Physiol.* 70, 21–23.
- Glasstone, S., 1946. *Textbook of Physical Chemistry*. Van Nostrand Co., New York, p. 289.
- Hagenmaier, R., 2002. The flavor of mandarin hybrids with different coatings. *Postharvest Biol. Technol.* 24, 79–87.
- Hagenmaier, R., 2004. Method for measuring internal gases of citrus fruit and determining peel permeance. *Proc. Fla. State Hort. Soc.* 116, 418–423.
- Hagenmaier, R.D., Baker, R.A., 1994. Internal gases, ethanol content and gloss of citrus fruit coated with polyethylene wax, carnauba wax, shellac or rosin at different application levels. *Proc. Fla. State Hort. Soc.* 107, 261–265.
- Hecht, C.E., 1990. *Statistical Thermodynamics and Kinetic Theory*. Dover Pub, Mineola, NY, p. 322.
- Ke, D., Kader, A.A., 1990. Tolerance of ‘Valencia’ oranges to controlled atmospheres as determined by physiological responses and quality attributes. *J. Am. Soc. Hort. Sci.* 115, 779–783.
- Stannett, V.T., 1985. The permeability of plastic films and coated papers to gases and vapors. *Tappi J.* 68 (9), 2–26.
- Weast, R.C., 1976. *Handbook of Chemistry and Physics*. CRC Press, p. 178.

Table 8
Mean ratios of internal gas volume to fruit weight

Type fruit	n	Ratio: internal gas vol./mass (L/kg)
‘Valencia’ oranges	54	0.12 ± 0.01
‘Fuji’ apples	59	0.19 ± 0.03
‘Red Delicious’ apples	42	0.21 ± 0.02
‘Lexington’ bell peppers	22	0.98 ± 0.04